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SYNTHESIS OF CARBON NANOTUBES (CNTs) USING SUPPORTED CATALYSTS

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ABSTRACT

Catalytic properties of cobalt (Co), ferrum (Fe) and mixture of cobalt and ferrum (Co-Fe) supported on aluminium oxides (Al_2O_3) and molecular sieves (MS) have been investigated in the synthesis of carbon nanotubes (CNTs). The supported catalysts were prepared by impregnation method. The supports were impregnated with metal salt solutions of Co, Fe or mixture of Co and Fe so as to get specific weight percentage of the metal on the supports. Acetylene is used as the source of carbon in inert condition. The pyrolysis of acetylene was carried out at temperature 700 °C. The effects of types of supports and catalyst, quantity of catalyst as well as the calcination process have also been studied. Types of Co or Fe metal compound formed on the support and the effect of calcination were determined by X-ray diffraction technique (XRD) and energy dispersive X-ray analysis (EDAX). Scanning electron microscope (SEM) and EDAX was used to study the quality and nature of as-grown CNTs. Results obtained showed that CNTs with different diameter sizes and form were produced from these types of supported catalysts.

Keywords: Carbon nanotubes (CNTs), X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM).

1. INTRODUCTION

The past decade has witnessed tremendous effort and progress in the field of carbon nanotubes. Ever since the discovery of carbon nanotubes by Iijima (1991), it has captured the attention of researchers worldwide. Understanding their unique properties and exploring their potential applications have been a main driving force for this area (Dresselhaus *et al.*, 2001, Daenen *et al.*, 2003, Saito *et al.*, 1998, Popov *et al.*, 2003).

Three relatively efficient methods to synthesize single wall carbon nanotubes have been identified: Laser ablation, carbon arc synthesis and chemical vapor deposition (CVD). Three of these methods depend on the use of catalysts. In each of these methods, carbon atoms self-assemble to form nanometer size tubes of carbon. However, all these methods need expensive equipment, complicated procedure for synthesis of catalysts as well as high power supply. Recently many material science researchers have turned their attention onto the development of simple, cheap and effective methods for the production of CNTs. Among these, catalytic

chemical vapour deposition (CCVD) seems to be one of the promising methods for synthesis of CNTs.

Controlled synthesis involving CCVD has been studied as an effective strategy to order or pattern CNTs on a variety of surfaces (Mukhopadhyay *et al.*, 2003). Metal and mixture of metals supported on oxides, clays and zeolites have been found to be active as catalysts in CCVD method (Nagaraju *et al.*, 2002). In the field of heterogeneous catalysis, a number of oxides and mixed oxides have been used to disperse and stabilize metallic particles. Catalytic properties of these solids are known to depend upon the interaction between the support and the metal particles, which in turn depends on their method of preparation. Therefore, it is interesting to investigate the influence of the support on the catalytic activity of metals in the synthesis of CNTs.

In the CCVD method, catalyst materials (usually transition metals such as Ni, Co and Fe) is heated to 500-1000 °C and exposed to hydrocarbon gas (methane, acetylene, etc.) flowing through the reaction zone. The dissociation of the gas occurs at the hot catalyst surface. The precipitation of carbon from the saturated metal particle leads to formation of tubular carbon structures in the form of nanotubes or nanofibers.

In this work, we have attempted to synthesize CNTs over Al_2O_3 or MS supported Fe, Co and Co-Fe catalysts. We will focus on the quantities and types of catalyst on the surfaces of Al_2O_3 and MS support. In addition, the effects of calcination to the supported catalysts are also investigated.

2. EXPERIMENTAL

2.1. Catalyst preparation

In this work, Al_2O_3 beads obtained from commercial source were used as catalyst support. Before the addition of catalyst onto the supports, the support was dried to eliminate water vapour and impurities. The catalysts were prepared by impregnation method. The support was immersed with either Co or Fe acetate salt solution (containing specific wt % of catalyst) until saturation and dried overnight. The prepared supported catalysts were then calcined at 450 °C for 17 hours and used in the synthesis of CNTs.

2.2. CNTs synthesis

For this purpose, a home-built reactor system has been designed. The reactor is a simple and low cost thermal catalytic chemical vapour deposition system. It is easy to handle and do not require expensive power supply and high pressure reaction chamber. The experiments to produce CNTs are carried out in a horizontal tube furnace at atmospheric pressure. The supported catalyst was spread in a ceramic boat, which was placed inside a vycor tube. Acetylene gas, C_2H_2 was passed through to react with the catalyst. The pyrolysis of C_2H_2 will be performed at temperature 700 °C. Prior to sampling, the reaction chamber was cooled down to room temperature. The samples were collected as black powder on the catalyst.

2.3. Characterization

The surface morphology and elements present on the support and catalysts were investigated using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDAX) (XL 40, Philips). The identification of metallic bulk crystallographic and amorphous phase present in the catalyst was carried out by X-ray Diffraction (XRD). The analyses of catalyst by XRD were conducted using Diffractometer D500 Siemens Crystalloflex with CuK_α (λ = 1.54060 Å) as the radiation source. The quality and nature of the as-grown CNTs were observed using SEM and EDAX.

3. RESULTS AND DISCUSSION

3.1. Al_2O_3 supported Co, Fe and Co- Fe catalysts

The quantity and quality of as-grown CNTs depend on the types and quantities of catalyst, the interaction between catalyst and support as well as the effect of calcinations on catalyst. From the XRD characterization, the Al_2O_3 support was determined as Al_2O_3 tetragonal, this material was found to be amorphous. The main peaks for Al_2O_3 tetragonal phase was observed at d values of 1.39141, 1.39566 and 2.73328 Å. After the impregnations of Co, the Co catalysts were detected as Co_3O_4 cubic, while Al_2O_3 tetragonal remained at the same phase, but it was observed that the structure of Al_2O_3 has been suppressed. The d values of Co_3O_4 cubic were assigned at 2.43473, 2.84993 and 2.01626 Å. The Al_2O_3 – Co catalyst after calcinations showed a similar diffraction pattern, *i.e.* Co_3O_4 cubic (Fig 1).

In the Al_2O_3 – Fe catalysts, the existence of Fe_2O_3 monoclinic as well as the Al_2O_3 tetragonal have been detected. In this case, the suppression of Al_2O_3 structure was not obvious. The Fe_2O_3 monoclinic phase is observed at d values of 2.72535, 1.38607 and 2.99200 Å. Calcination of Al_2O_3 – Fe catalysts have not gained any formation of new phases (Fig. 1).

Interestingly, the X-ray diffractograms of Al_2O_3 – Co - Fe catalysts showed the existence of both Co and Fe in their individual phase, i.e. Co_3O_4 cubic and Fe_2O_3 monoclinic, indicating no interaction between the two catalysts. The structure of Al_2O_3 was suppressed by the existence of Co catalyst. The d values for Co_3O_4 cubic were detected 2.42536, 2.85037 and 2.01005 Å, while the Fe_2O_3 monoclinic phase was observed at d values of 2.73032, 1.38627 and 2.98036 Å. Calcination did not give any significant change to the Co - Fe catalysts, both of the Co and Fe have remained as Co_3O_4 cubic and Fe_2O_3 monoclinic as shown in figure 1.

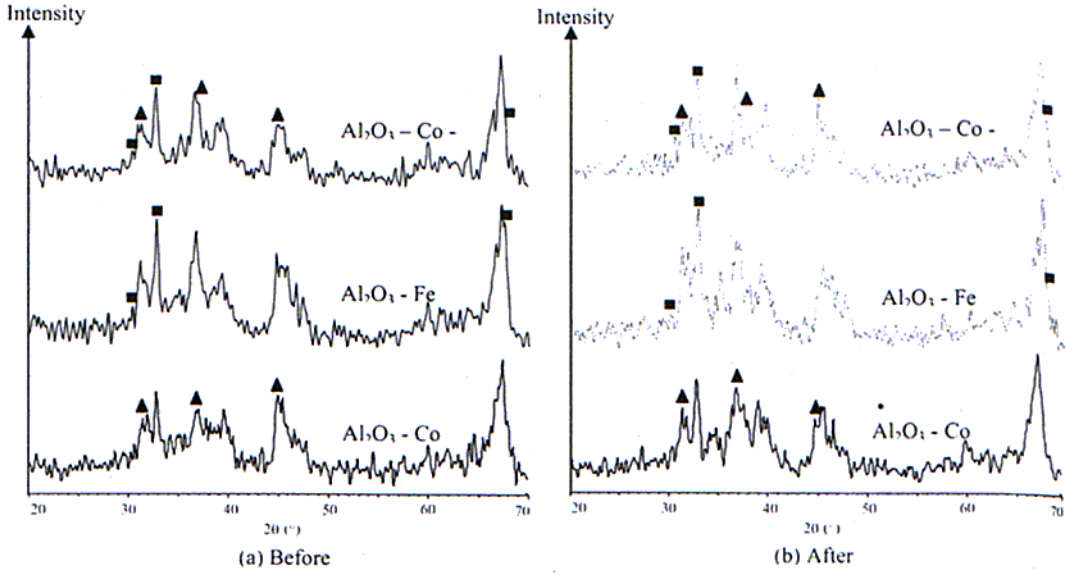

Figure 1. The X-ray diffractograms of Al_2O_3 supported catalysts, (a) before calcinations and (b) after calcinations, ▲ : Co_3O_4 cubic and ■ : Fe_2O_3 monoclinic.

From figure 1, it is observed that in all of the catalysts, the Al_2O_3 structure did not collapse after impregnation and calcinations. This indicated that the Al_2O_3 is a suitable support for Co, Fe and Co – Fe catalysts. Apart from that, all the supported catalysts remained in the same phases (Co_3O_4 cubic and Fe_2O_3 monoclinic) after calcinations. Therefore, the support and catalysts are thermally stable and appropriate for reaction of CNTs synthesis at high temperature.

All of the Co, Fe and Co-Fe catalysts were found to be effective in the formation of CNTs. The EDAX analyses indicated that the quantity of Co catalysts was in the range of 3.5 wt % to 11.5 wt % and the quantity of Fe catalyst varied from 7.1 wt % to 16.2 wt %. While, the mixture of Co and Fe catalysts contained between 4.2 – 5.4 wt % of Co and 4.2 – 13.2 wt % of Fe. As a result from the EDAX analyses, the carbon content of all as-grown CNTs samples were found to be > 25 wt %. Therefore, this indicates that the Al_2O_3 supported catalysts were effective in CNTs growth. Table 1 showed the carbon content of as-grown CNTs samples. It was noticed that the yield of Fe catalysts were higher than Co catalyst, but the Co – Fe catalysts gave the highest yield. This can be seen clearly from the SEM micrographs (figure. 2).

Table 1. The carbon content (wt %) of CNTs grown over Al_2O_3 supported catalysts.

Catalysts	Carbon content (wt %)	
	Before calcination	After calcination
Al_2O_3 – Co	25.0 – 42.3	44.6 – 45.7
Al_2O_3 – Fe	39.3 – 45.9	39.4 – 54.3
Al_2O_3 – Co - Fe	53.5 – 73.8	45.1 – 72.0

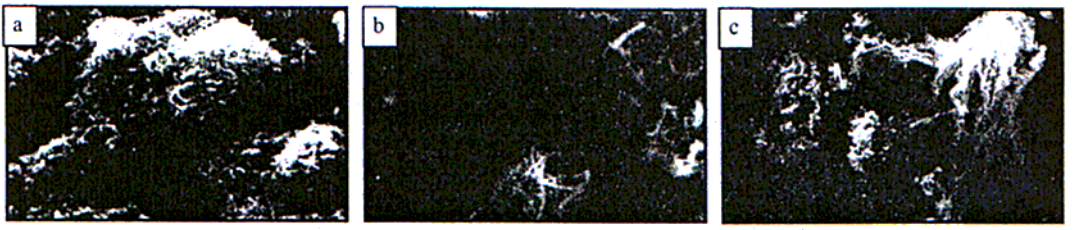

Figure 2. The SEM micrographs of as-grown samples on three types of supported catalyst (10000 ×), (a) Al_2O_3 – Co, (b) Al_2O_3 – Fe and (c) Al_2O_3 – Co – Fe.

The quantity of the as-grown CNTs was relative to the amount of catalyst. The higher percentage of the catalyst, the higher the density of the CNTs obtained. Fig. 3 showed the SEM micrographs of two as-grown CNTs with different quantity of Co catalyst. Fig. 3(a) showed the sample with lower percentage of Co. As proposed by many researchers, the surface active sites of the metal particles of the catalyst can help in the adsorption and decomposition of hydrocarbon molecules (Chen *et al.*, 1997). It is obvious that CNTs grown over Co catalyst are relatively small, uniform in diameter and in the form of bundles.

Figure 4(a) and 4(b) showed the SEM micrographs of CNTs grown over Al_2O_3 – Fe catalyst before and after calcinations respectively. It is observed that the CNTs grown over the calcined catalyst were denser with uniform diameter. Here, we noticed that the calcination help to improve the catalytic activity in CNTs growth. It is interesting to note that from the images of CNTs grown over Co-Fe catalysts, aligned CNTs were observed (Fig. 5). The quasi-alignment CNTs is high in purity with uniform diameter distribution. According to Mukhopadhyay [6], the presence of Fe coupled with Co could be responsible for the quasi-alignment of CNTs.

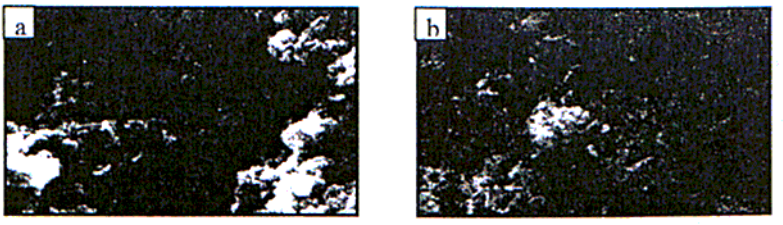

Figure 3. The SEM micrographs of as-grown CNTs from Al_2O_3 – Co catalyst (10000 ×), (a) sample with lower quantity of Co and (b) sample with higher quantity of Co.

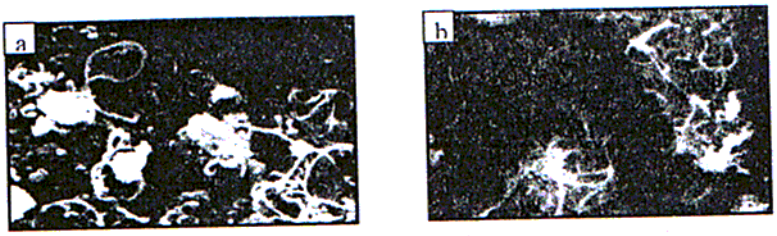

Figure 4. The SEM micrographs of as-grown CNTs from Al_2O_3 – Fe catalysts (10000 ×), (a) sample before calcination, (b) sample after calcination.

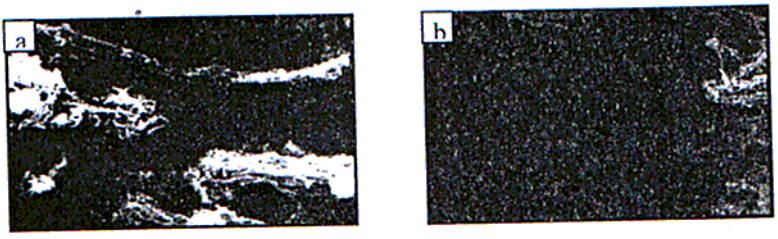

Figure 5. The SEM micrographs of as-grown CNTs from Al_2O_3 – Co - Fe catalysts (10000 ×), (a) sample before calcinations, (b) sample after calcination.

3.2. MS Supported Co, Fe and Co- Fe Catalysts

From the X-ray diffraction analyses, the molecular sieves support was identified as mixtures of $K_{11}Si_{12}Al_{12}O_{48}$ cubic and $NaSiAlO_4$ cubic, these materials were found to be crystalline. The d values of $K_{11}Si_{12}Al_{12}O_{48}$ cubic were observed at 12.44060, 8.72760 and 3.71963 Å. The main peaks for $NaSiAlO_4$ cubic phase were assigned at 12.44060, 8.72760 and 7.1144 Å.

After the impregnation of Co, the Co catalysts on MS were found to be stable in the form of $Co_{.333}Na_{.333}(AlSiO_4)(H_2O)_{2.92}$ cubic, which the main peaks observed at 12.3594, 8.70770 and 3.71415 Å as shown in Fig. 6. The MS- Co catalyst after calcinations has a similar diffraction pattern, *i.e.* $Co_{.333}Na_{.333}(AlSiO_4)(H_2O)_{2.92}$ cubic (figure). The XRD diffractograms of MS supported Fe catalyst showed that Fe catalyst was stable in the form of $Fe_{2.7}Na_{2.0}(Si_{12}Al_{12}O_{48})(H_2O)_{14.8}$ cubic. The $Fe_{2.7}Na_{2.0}(Si_{12}Al_{12}O_{48})(H_2O)_{14.8}$ cubic phase was observed at d values of 12.35952, 8.72726 and 3.70611 Å. (Fig. 6). In the MS supported Co – Fe catalyst, the Co and Fe catalyst existed in their individual phase, *i.e.* $Co_{.333}Na_{.333}(AlSiO_4)(H_2O)_{2.92}$ cubic and $Fe_{2.7}Na_{2.0}(Si_{12}Al_{12}O_{48})(H_2O)_{14.8}$ cubic, point out that no interaction between the Co and Fe catalyst (figure. 6).

The incorporation of either Co or Fe on MS support does not change the structure of MS while the calcination process did not give any changes to the Co and Fe catalysts phases. This implied that the MS is a suitable support for Co, Fe and Co – Fe catalysts. All of the MS supported catalysts remained in the same phases after calcinations (figure 6), from here we

noticed that the support and catalysts are thermally stable and suitable for the synthesis of CNTs at high temperature. Apart from that, all the phases of compounds were in cubic form, therefore, most of the peaks in X-ray diffractograms were overlapping to each other, resulting high intensity of the peaks.

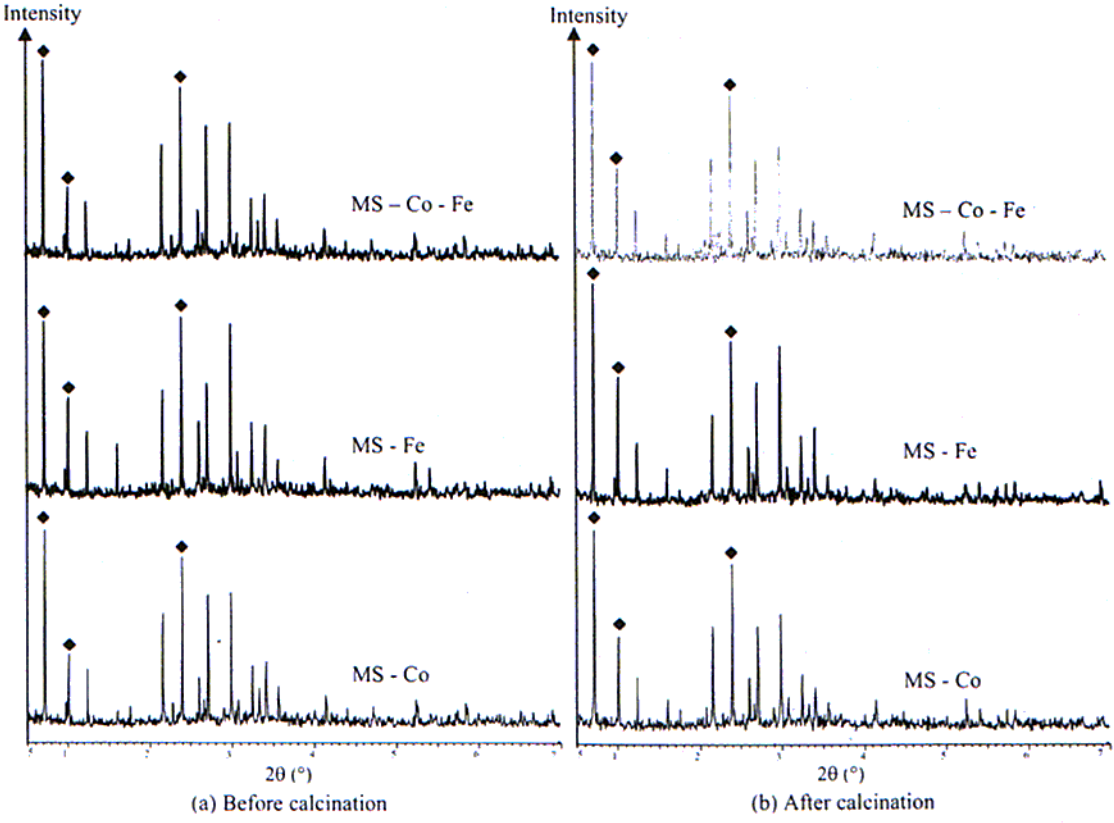

Figure 6. The X-ray diffractograms of MS supported catalysts, (a) before calcinations and (b) after calcinations.
◆ : $Co_{.333}Na_{.333}(AlSiO_4)(H_2O)_{2.92}$ cubic and $Fe_{2.7}Na_{2.0}(Si_{12}Al_{12}O_{48})(H_2O)_{14.8}$ cubic.

The EDAX analyses showed that the amounts of Co catalysts and Fe catalysts on MS support were in the range of 4.8 – 14.4 wt % and 6.8 – 18.3 wt % respectively. The Co–Fe catalysts are also contained 4.2 – 5.4 wt % of Co and 6.1 – 13.2 wt % of Fe. It is observed that the calcination process did not give any significant changes to the quantity of the catalysts. The EDAX analyses depict that the carbon content of all as-grown CNTs samples were in the range of 25.0 wt % to 72.7 wt %, the data were tabulated in Table 2.

Fig 7(a) and (b) showed the SEM micrographs of CNTs grown over MS – Co catalyst. Before calcination, the length of as-grown CNTs was between 2.5 to 2.9 μm, in the form of bundles with uniform diameter. The existence of CNTs in the form of coils has also been observed (figure(a)). After the calcination, the length of as-grown CNTs was found to be longer (4.9 – 6.5 μm) with smaller diameter (figure 7 (b)).

According to Liu *et al.* (2004), the growth of CNTs ia affected by the morphology and particle size of catalyst. High quality CNTs can only be grown with the assistance of suitable morphology and particle size of Fe catalyst. Figure 8 (a) showed the SEM images of MS – Fe catalyst, Fe nanoparticles with cube shaped can be observed. This cube shape particles benefit the growth of CNTs with high density and purity (figure 8 (b)).

It is interesting to note that when MS support had a mixture of Co and Fe, a very high density of CNTs was observed, as shown in figure. 9 (a). The CNTs formed have very long length, possessed high purity and uniform diameter. The existence of aligned CNTs was also observed (figure 9 (b) & (c)).

Table 2: The carbon content (wt %) of as-grown CNTs over MS supported catalysts.

Catalysts	Carbon content (wt %)	
	Before calcination	After calcination
MS – Co	24.8 – 25.0	28.1 – 32.4
MS – Fe	30.4 – 32.7	22.5 – 45.1
MS – Co - Fe	47.7 – 61.8	48.5 – 72.7

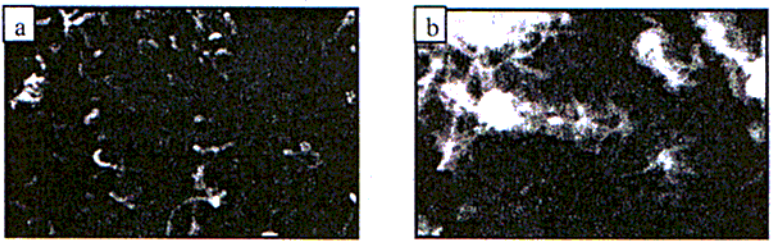

Figure 7. The SEM micrographs of as-grown CNTs from MS – Co catalysts (10000 ×), (a) sample before calcinations, (b) sample after calcination.

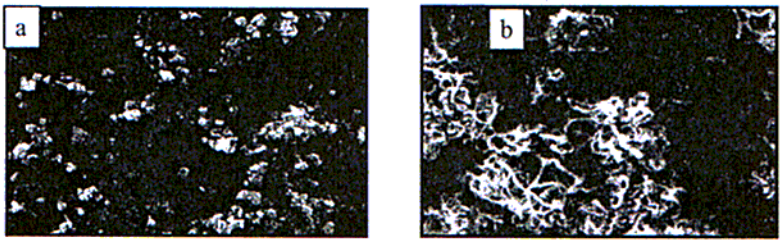

Figure 8. The SEM micrographs: (a) MS – Fe catalyst before synthesis of CNTs (1000 ×), (b) as-grown CNTs over MS – Fe catalyst (10000 ×).

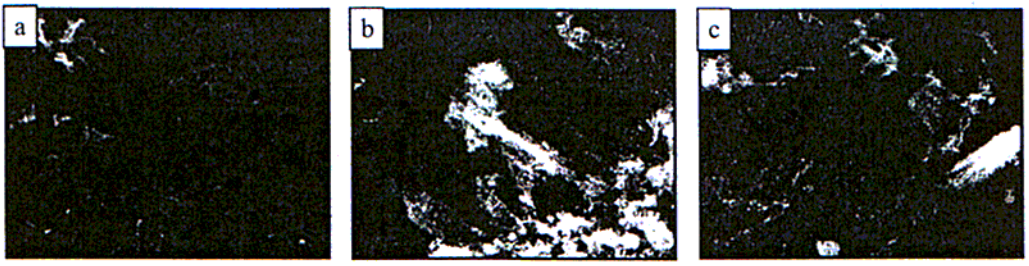

Figure 9. The SEM micrographs of as-grown CNTs over MS – Co – Fe catalysts different quantity of Co and Fe. (a) High density CNTs, (b) and (c): aligned CNTs.

3.3. Comparison between Al_2O_3 Supported Catalysts and MS Supported Catalysts

In this work, there is no purification process required. The as-grown samples have been directly used for SEM analyses. The SEM micrographs clearly revealed that the as-grown CNTs (over Al_2O_3 and MS supported catalysts) have high degree of purity and density.

It is well established that the catalyst support plays an important role in determining the catalytic activity of a metal present in it. The state of the metal on a support depends on the kind of metal-support interaction, which in turn depends on the nature of the support. Nagaraju (2002) also reported that alumina-silica systems containing 20 wt % of Al showed very high activity towards MWNTs formation. This fact explained that MS supported catalysts gave better performance in CNTs growth, compared to the Al_2O_3 supported catalyst. Mukhopadhyay et al. (2003) have reported that the supports as well as the nature of metal(s) play major roles for the CNT's alignment. Although the catalysts impregnated on Al_2O_3 and MS are the same, but their behaviour for getting the alignment is different. Amongst all the catalysts, only Co – Fe supported catalysts contribute to the alignment of as-grown CNTs, with Al_2O_3 – Co – Fe gave higher degree of alignment. This reflects that a good combination of metals is also a major factor for achieving the alignment of carbon nanotubes.

4. CONCLUSION

All the Al_2O_3 and MS supported catalyst are effective in producing CNTs in different forms, such as bundles and aligned CNTs. However, the use of supported Co – Fe catalysts gave the best quality yield with higher purity and alignment.

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